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54 A method for the treatment of pulp.

57 The invention relates to a method for improving the drainability of mechanical pulp or pulp mainly containing mechanical pulp by means of enzyme treatment by adding to the pulp at least one hemicellulose-dissolving enzyme or an enzyme preparation containing at least one hemicellulose-dissolving enzyme and being substantially free from cellulose-dissolving enzymes. The enzyme treatment according to the invention not only improves the drainability of the pulp but also retains the strength properties of the pulp since no cellulose-dissolving enzymes are used.

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A method for the treatment of pulp

The invention relates to a method for improving the drainability of mechanical pulp, such as a thermomechanical or deinked pulp, by treating the pulp by a hemicellulose-hydrolyzing enzyme.

The drainability of pulp is usually described by the freeness value. It is known that mechanical treatment and deinking deteriorate the drainability of pulp. The use of deinked pulp in particular is restricted due to its poor drainability. During mechanical treatment, a fibre is exposed to stresses, which results in an abundant formation of fine-grained material. For this reason, the drainage properties of finished pulp are not at optimum, which appears as a decreased freeness value. In many cases, the drainage properties, i.e. the practical value of a pulp would be substantially increased if the freeness value could be improved by 10 to 20 units.

In the production of mechanical pulp, fibres are separated from wood mechanically by means of heat only without any addition of chemicals. The fibre is thereby subjected to stresses so that the lignin binding the fibres together is softened. Under continued mechanical stress, the elasticity of lignin fails and the fibres are detached from each other.

Mechanical pulps include groundwood pulp, refiner mechanical pulp, pressure groundwood pulp and thermomechanical pulp. In the production of the different kinds of mechanical pulp, the required temperature rises in the above order, being at its lowest in the production of groundwood pulp and at its highest in the production of thermomechanical pulp.

The higher the processing temperature, the less damaged the detached fibres are; however, the surfaces of the fibres are covered with lignin in an increasing degree. It is typical of mechanical processing of pulp that plenty of fine-grained material (noil fibre) is formed. This is not the case with chemical processing, in which lignin is dissolved chemically. To a certain extent, fine-grained material is of advantage to strength properties whereas it affects adversely the drainage properties of pulp.

With groundwood pulp, the negative and positive properties of fine-grained material are substantially balanced, whereas the potential strength properties of thermomechanical pulp in particular are clearly superior to the drainage properties. However, the strength properties of groundwood pulp are relatively poor as compared with the properties of thermomechanical pulp.

Today so called recycled pulp is also used as paper raw material. Recycled pulp is manufactured of waste paper, whereby wood fibre utilized at least once in the form of paper is reused. The main function of a recycled pulp process is to remove impurities contained in waste paper. Methods used for this purpose can be divided into three groups:

- 1) mechanical methods,
- 2) methods based on the use of heat,
- 3) chemical methods.

Recycled pulps can be deinked, if desired. The basic idea of deinking is to separate ink from the fibre chemically and mechanically and to bring the separated ink to a hydrophilic state in a fibre-water slush. The separated ink can be removed from the slush by flotation and/or by washing.

A deinking plant uses as raw material two kinds of waste paper: home waste paper and newsprint waste. Home waste paper is unsorted and its composition varies. It typically contains 60 to 70% of newsprint, 20 to 30% of magazine paper and less than 10% of various kinds of paperboard and cardboard.

On the basis of the above, it can be calculated that a major part of the original mass of deinked pulp consists of mechanical pulp (newsprint containing 85 to 100% and magazine paper 70 to 90% of mechanical pulp). Furthermore, it is typical of the production of recycled pulp that it always requires mechanical energy for defibering the paper, as a result of which, in addition to the desired effect, fine-grained material is formed. The disadvantages fine-grained material are particularly outstanding in deinked pulp because mechanical energy was needed to the removal of ink, too.

All the pulp types mentioned above contain plenty of fine-grained material, but it is especially thermomechanical pulp and deinked pulp that have poor drainage properties as compared with their usability in general.

The properties of a particular pulp can be affected by various enzymatic treatments. However, results to be obtained by such treatments are generally difficult to predict. In most cases, combinations of different enzyme activities have to be used while avoiding undesired enzyme activities.

Prior art discloses the following successful applications:

French Patent Specification 2,557,894 discloses a method in which chemical pulp is subjected to treatment with xylanase enzyme with the purpose of reducing the beating time. Canadian Patent Specification 758,488 relates to a method in which the beatability of pulp is improved by a cellulase/pectinase/lipase

enzyme treatment. French Patent Specification 2,571,738 in turn discloses a method in which pulp is provided with special properties by cellulase treatment. Japanese Patent Specification 60,126,395 discloses a method for improving the beating process by enzyme addition.

Japanese Patent Specification 59,009,299 discloses a method in which alkaline cellulase and a surface-active agent are added to a deinking process for making the removal of ink more efficient.

Japanese Patent Application 63,059,494 discloses a method for improving the whiteness of recycled pulp by means of alkaline cellulase.

French Patent Application 8,613,208 discloses a method for improving the properties of previously beaten pulp, such as recycled pulp having a Schopper-Riegler (SR) number exceeding 25, by means of a cellulase/hemicellulase treatment. According to the application, the SR number can be decreased without affecting adversely the other properties of the pulp. The SR number describes the drainability of pulp; the lower the SR value, the better the rate of dewatering is.

Said application describes mainly the treatment of recycled pulps containing plenty of chemical pulp. On applying the enzyme treatment according to said application to recycled pulps containing mainly mechanical pulp, it has been found that treatment with enzyme mixtures containing substantial amounts of cellulase deteriorates the strength properties of the pulp; this appears from the examples set forth below. The strength values are decreased even by minor amounts of cellulase especially if the pulp containing enzymes has to be stored for longer periods of time on account of process disturbances, for instance. Therefore it is preferable that the enzyme used in the treatment does not affect adversely the strength properties of pulp, not even during a long time of action (several hours).

The object of the present invention is to improve the drainability of mechanical pulp, particularly thermomechanical and/or deinked pulp, by means of enzyme treatment while maintaining the strength properties of the pulp.

The invention is characterized by adding to mechanical pulp or to pulp mainly containing mechanical pulp, such as thermomechanical or deinking pulp, at least one hemicellulose-dissolving enzyme or an enzyme preparation containing at least one hemicellulose-dissolving enzyme and being substantially free from cellulose-dissolving enzymes. The addition of enzymes can be carried out in connection with the acidification of the pulp or thereafter.

Hemicellulose-dissolving enzymes include xylanases, beta xylosidase, acetyl esterase, alpha arabinosidase, alpha glucuronidase, arabinases and mannanases.

Particularly preferred enzymes are xylanases and mannanases.

Enzymes suited for the application according to the invention include hemicellulases and hemicellulase preparations, especially xylanases and mannanases, which are substantially free from cellulases. As used herein the term "cellulases" refers to enzymes which are able to dissolve crystalline cellulose and to liberate therefrom remarkable amounts of sugars or oligosaccharides. As known, enzymes referred to in the invention are produced e.g. by actinomycetes (such as Streptomyces olivochromogenes), bacteria (such as Bacillus sp.) and fungi (such as Penicillium stecklii).

A suitable enzyme dosing is about 30 to 200,000 units/kg on the dry content of the pulp, preferably about 100 to 50,000 units/kg. The treatment can be carried out within the pH range from about 2 to about 10, preferably from about 4 to about 8, depending e.g. on the origin and properties of the used hemicellulase enzyme. The treating time depends on the enzyme dosage and the treatment conditions, ranging from 10 minutes to one day, preferably from half an hour to 8 hours. The temperature during the enzyme treatment may vary from about 10 to about 90°C, preferably from about 25 to 70°.

The xylanase activity of the enzyme preparations was determined as follows:

To 1 ml of xylan solution (1%, Sigma No: X-0376, prepared in 50 mM Na citrate buffer, pH 5.3), 1 ml of an enzyme suitably diluted in the same buffer was added. The solution was incubated at +50°C in a water bath for 30 minutes. The reaction was stopped by adding 3 ml of DNS reagent (3,5-dinitrosalicylate reagent), and the colour was developed by cooking the sample for 5 minutes. The absorbance was measured at a wave length of 540 nm. One enzyme unit liberates one micromole of reducing sugars calculated as xylose per one minute under the assay conditions.

The mannanase activity of the enzyme preparations was determined as follows:

To 1 ml of locust bean gum solution (0.5%, Sigma No: G-0753, prepared in 50 mM Na-citrate buffer, pH 5.3) 1 ml of an enzyme suitably diluted in the same buffer was added. The solution was incubated at +50°C in a water bath for 10 minutes. The reaction was stopped by adding 3 ml of DNS reagent, and the colour was developed by cooking for 5 minutes. The absorbance was measured at a wave length of 540 nm. One enzyme unit liberates one micromole of reducing sugars calculated as mannose per one minute under the assay conditions.

The cellulase activity of the enzyme preparations was determined as filter paper activity (Ghose T.K. et

al., Symposium of Enzymatic Hydrolysis of Cellulose, Bailey M., Enari T.M., Linko M., Eds. (SITRA, Aulanko, Finland, 1975), p. 111 to 136):

A piece of filter paper (Whatman 1, 50 mg) was added to 1 ml of acetate buffer (0.05 M NaAc, pH 4.8). 1 ml of a suitably diluted enzyme solution was added. The solution was incubated for one hour at 50°C. The reaction was stopped by adding 3 ml of DNS reagent, and the colour was developed and measured as in the xylanase determination. One activity unit liberates 1 micromole of reducing sugars calculated as glucose per one minute.

The method according to the invention will be illustrated by means of the following examples. The following enzyme preparations were used in the examples:

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Enzyme preparation 1

15 (cellulase preparation)

MULTIFECT L 250 (commercial preparation, Finnsugar Ltd, prepared by the mold Trichoderma longibrachiatum activity: xylanase 250 units/g, cellulase about 100 units/g)

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Enzyme preparation 2

(cellulase/hemicellulase preparation,

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MULTIFECT K (commercial preparation), Finnsugar Ltd, prepared by the fungus Trichoderma longibrachiatum; activity: xylanase 6,000 units /g, cellulase 30 units/g)

Enzyme preparation 3

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(hemicellulose preparation)

Xylanase preparation (pre-pared by actinomycete Streptomyces olivochromogenes using the method described in Evaluation of Different Microbial Xylanolytic Systems, Poutanen, K., Rättö M., Puls, J. and Viikari, L., Journal of Biotechnology, 6 (1987) 49-60)

In the method according to the invention, preparation 3 represents a useful enzyme preparation containing hemicellulose-dissolving enzyme (xylanase) and being substantially free from cellulose-dissolving enzymes. Preparations 1 and 2 are reference preparations, which in addition to the hemicellulose activity contain varying amounts of cellulose-dissolving enzyme activities.

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Example 1

An aqueous slurry having a dry matter content of 10% was prepared from dried delinked pulp (Keräyskuitu Oy, export grade) and allowed to stand overnight at room temperature. The slurry was then diluted with water to a dry content of 5% and defibered in a laboratory mixer (3,000 rpm, 15 min). The pH of the slurry was adjusted from the initial pH of about 7 to 5.4 by means of 1 M sulphuric acid.

3 kg of the slurry was weighed for the test and it was heated to +50°C. The temperature was maintained by keeping the vessel containing the slurry in a water bath. The enzyme preparation to be tested was added to the slurry sample in amounts appearing from Table 1, and the solution was mixed thoroughly. Sample batches of 1 kg were taken from the sample after 1, 2 and 5 hours.

After enzyme treatment the drainability of the pulp was determined as the freeness value, and recirculated water sheets were prepared for the strength and colour measurement. The sheets were prepared by means of a mould called a recirculated water sheet mould according to the standards of the Finnish Pulp and Paper Research Institute. All the tests were carried out according to the standardized test procedure SCAN. The results are shown in Table 1. The control sample was treated similarly as the test samples except that no enzyme was added. The added amounts of enzyme are given as enzyme units per

one kg calculated on the dry substance of the pulp.

Table 1

Results from the enzyme treatment				
Sample	Enzyme 1	Enzyme 2	Enzyme 3	Control
Xylanase content (units/kg)	250	6000	5000	-
Cellulase content (units/kg)	100	30	-	-
Freeness (ml)				
0 h	148	148	148	148
1 h	149	141	161	150
2 h	163	146	170	152
5 h	184	164	164	151
Tear index (mN m ² /g)				
0 h				
1 h	5.6	6.0	6.9	6.6
2 h	5.0	5.7	6.1	6.3
5 h	4.6	5.3	6.3	6.8
ISO brightness (%)				
0 h				
1 h	54.1	54.1	54.2	54.0
2 h	54.1	54.1	54.3	54.3
5 h	54.1	54.3	54.4	54.3
Tensile index (N.m/g)				
1 h	29.5	30.1	29.9	29.7
2 h	28.8	29.8	29.6	30.6
5 h	27.1	28.4	29.1	30.8
Light scattering coefficient (m ² /kg)				
1 h	53.0	52.4	53.9	53.6
2 h	53.7	53.4	53.7	52.9
5 h	54.6	53.3	55.7	53.9
Air resistance (s)				
1 h	39	49	39	38
2 h	36	53	39	43
5 h	28	41	38	49
Density (kg/m ³)				
1 h	421	430	421	420
2 h	421	440	420	417
5 h	416	431	423	430
Ash content (%)				
1 h	4.59	4.55	4.80	4.50
2 h	4.60	4.63	4.78	4.73
5 h	4.58	4.62	4.79	4.96

The use of hemicellulase clearly improved the properties of the pulp: both xylanase and cellulase improved the drainability whereas cellulase simultaneously clearly deteriorated the tear index. The enzyme treatment did not affect adversely the other properties of the pulp.

Example 2

The tests were carried out similarly as in Example 1. Enzyme 3 (xylanase) only was tested. The results are shown in Table 2.

Table 2

Results from the enzyme treatment		
Sample	Enzyme 3	Control
Xylanase content (units/ kg)	5000	-
Freeness (ml)		
0 h	147	147
1 h	167	148
2 h	168	151
5 h	167	150

The hemicellulase treatment clearly improved the drainability of the pulp.

Example 3

The tests were carried out similarly as in Examples 1 and 2. However, the amount of the added xylanase preparation (enzyme preparation 3) was smaller. Samples were taken after half an hour, one hour and four hours. The results are shown in Table 3.

Table 3

Results from the enzyme treatment			
Sample	Enzyme 1	Enzyme 3	Control
Xylanase content (units/kg)	250	1250	-
Cellulase content (units/kg)			
Freeness (ml)			
0 h	160	160	160
0.5 h	158	-	156
1 h	165	170	155
4 h	-	182	166
Tear index (mN m ² /g)			
0 h	6.5	6.5	6.5
0.5 h	6.1	-	6.5
1 h	5.8	6.5	6.6
4 h	-	6.6	6.3
ISO brightness (%)			
0 h	57.6	57.6	57.6
0.5 h	57.3	-	57.6
1 h	57.4	57.7	57.6
4 h	-	58.0	57.9

The results correspond to those obtained in Example 1. The xylanase treatment improved the

properties of the pulp. Even though its time of action was shortened, cellulase nevertheless degraded the strength properties of the pulp.

8 Example 4

Unbleached, unacidified deinked pulp (Keräyskuitu Oy) having a dry matter content of about 7.5 % was allowed to stand overnight, whereafter it was diluted to a concentration of 20 g/l and was defibred and beaten in a hollander to a freeness value of 130. After the beating, the pH was adjusted to 5.5 by 1 M H_2SO_4 .

Xylanase enzyme preparation (enzyme preparation 3) was added to the pulp in amounts that appear from Table 4. The pulp was heated by means of a steam coil to 50°C and it was incubated at 50°C in a water bath. The freeness was determined after the pulp had been incubated one hour and four hours. The results are shown in Table 4.

Table 4

Results from the enzyme treatment			
Sample	Enzyme 3	Enzyme 3	Control
Xylanase content (units/kg)	500	1250	-
Cellulase content (units/kg)	-	-	-
Freeness (ml)			
0 h	142	142	142
1 h	154	158	141
4 h	153	163	141

It can be seen from the results that the xylanase enzyme preparation free from cellulase activity increases the freeness value of an unbleached, unacidified deinked pulp by 11 to 21 units depending on the dosing.

35 Example 5

Bleached, acidified (pH 7.7) deinked pulp (Keräyskuitu Oy, normal grade) having a dry matter content of about 10% was allowed to stand overnight, whereafter it was diluted to a concentration of 20 g/l and defibred by a hollander. After defibering the pH was adjusted to 5.5 by 1 M H_2SO_4 , whereafter beating was carried out. The freeness of the pulp before beating was 199 and after a beating time of 5 minutes 131.

Xylanase enzyme preparation (enzyme preparation 3) was added to the pulp in amounts that appear from Table 5. The pulp was heated by means of a steam coil to 50°C and it was incubated at 50°C in a water bath. The freeness value was determined after the pulp had been incubated for one hour and four hours, respectively. The results are shown in Table 5.

Table 5

Results from the enzyme treatment			
Sample	Enzyme 3	Enzyme 3	Control
Xylanase content (units/kg)	500	1250	-
Cellulase content(units/kg)	-	-	-
Freeness (ml)			
0 h	131	131	131
1 h	142	145	131
4 h	149	144	133

It can be seen from the results that the xylanase enzyme preparation free from cellulase activity increases the freeness value of a bleached, unacidified deinking pulp by 10 to 15 units depending on the dosing.

Example 6

Further embodiments

When the enzyme is applied in an integrated plant, i.e. in a plant in which either a plant producing mechanical pulp or a deinking plant is connected to a paper mill, the enzyme addition can be carried out before the pulp is transferred to a paper machine. If the above-mentioned deinking plant is not integrated with a paper mill, the enzymes can be added to the slurry of the pulp and then allowed to act a suitable period of time, whereafter the pulp is dried and after-treated as desired. Enzymes can be alternatively added to the pulp slurry at the paper mill and then allowed to act, if the pulp has been purchased from elsewhere.

Enzyme treatment is also suitable for chemimechanical pulp, in which the separating of fibres is mainly carried out mechanically while using a weak chemical dosage as an aid for softening the lignin. A typical example of such pulp is CTMP pulp (chemical thermomechanical pulp).

The foregoing general discussion and experimental examples are intended to be illustrative of the present invention, and are not to be considered as limiting. Other variations within the spirit and scope of this invention are possible and will present themselves to those skilled in the art.

Claims

1. A method for improving the drainability of mechanical pulp or pulp mainly containing mechanical pulp by means of enzyme treatment, **characterized** by adding to the pulp at least one hemicellulose-dissolving enzyme or an enzyme preparation containing at least one hemicellulose-dissolving enzyme and being substantially free from cellulose-dissolving enzymes.
2. A method according to claim 1, **characterized** in that the mechanical pulp is thermomechanical pulp.
3. A method according to claim 1, **characterized** in that the mechanical pulp is deinked pulp.
4. A method according to claim 1 or 3, **characterized** in that the addition of the enzyme /enzymes is carried out in connection with or after the acidification of the pulp.
5. A method according to any of the preceding claims, **characterized** in that the hemicellulose-dissolving enzyme or enzyme preparation is added in an amount of about 30 to about 200,000 enzyme units/kg calculated on the dry substance of the pulp.
6. A method according to claim 5, **characterized** in that the hemicellulose-dissolving enzyme or enzyme preparation is added in an amount of about 100 to about 50,000 enzyme units/kg calculated on the dry substance of the pulp.
7. A method according to any of the preceding claims, **characterized** in that xylanase or xylanase preparation substantially free from cellulose-dissolving enzymes is added to the pulp.
8. A method according to any of the preceding claims, **characterized** in that mannanase or mannanase

preparation substantially free from cellulose-dissolving enzymes is added to the pulp.

9. A method according to any of the preceding claims, **characterized** in that the enzyme treatment is carried out within the pH range from about 2 to about 10.

10. A method according to claim 9, **characterized** in that the enzyme treatment is carried out within the pH range from about 4 to about 8.

11. A method according to any of the preceding claims, **characterized** in that the enzyme treatment is carried out at about 10 to 90°C.

12. A method according to claim 11, **characterized** in that the enzyme treatment is carried out at about 25 to 70°C.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	FR-A-2 604 198 (LA CELLULOSE DU PIN) * Page 3, lines 19-24; page 4, lines 15-31 * ---	1-4,7, 10,12	D 21 C 9/00 C 12 S 3/08
D,Y	FR-A-2 557 894 (CENTRE TECHNIQUE DE L'INDUSTRIE DES PAPIERS, CARTONS ET CELLULOSES) * Page 2, line 23 - page 4, line 14 * ---	1-4,7, 10,12	
A	TAPPI, vol. 65, no. 6, June 1982, pages 93-96, Atlanta, Georgia, US; L. PILON et al.: "Increasing water retention of mechanical pulp by biological treatments" -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 21 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-09-1989	Examiner SONGY O.M-L.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			